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TITLE CALCULATED PROPERTIES AND SORPTION BEHAVIOR OF VARIOUS MOLECULES

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## CALCULATED PROPERTIES AND SORPTION BEHAVIOR OF VARIOUS MOLECULES

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### ABSTRACT

We are investigating the relationships between several fundamental molecular properties and a molecule's observed sorption behavior on substrates such as charcoal, which often parallel the molecule's boiling point. We show that the boiling points of a large range of molecules can be predicted from the polarizability, size and dipole moment of the molecules. A more detailed model of the electrostatic and polarization interactions is developed using atom centered multipole expansions (ACME's) of the electron density distribution of a molecule, which is derived from *ab initio* calculations. We show that these interactions are extremely important for polar molecules and/or substrates, and that they also play a role for "non-polar" molecules such as benzene or ethylene.

### INTRODUCTION

The physisorption of a molecule on a surface results from intermolecular forces between the two species. These forces are typically divided into the four classes of dispersion, polarization (induction), electrostatic and exchange-repulsion. The energies of interaction that result from these forces will depend upon the relative orientation of the two species and their specific attributes. The polarizability and electrostatic properties of a molecule are particularly important since they contribute to the dispersion, polarization and electrostatic forces. These constitute the attractive interactions and will determine how tightly bound a sorbent will be.

We are particularly interested in the adsorption on charcoal, which is a major component of many filtering systems. There are a wide variety of charcoals available which differ in their source material and subsequent treatment, and these exhibit different absorption characteristics. In addition, the charcoal surface is poorly characterized, being very heterogeneous and containing numerous non-carbon "impurities" which undoubtedly play important roles in determining a material's unique sorption properties. In order to mimic such an irregular system, an extremely flexible model will be required. We are developing such a model based upon atom centered potentials, since this allows us to construct a model surface atom-by-atom. We describe here our results in developing this model for the polarizability and electrostatic properties of various molecules and the roles of these in the sorption process.

### RESULTS AND DISCUSSION

We have previously shown that sorption properties can often be related to the boiling point of the sorbent molecule<sup>2</sup>. An example of this is given in Figure 1 which shows the relationship

between the capacity of a charcoal bed at a challenge concentration of 680 ppm,  $Q(680)$ , and the boiling point, BP ( $^{\circ}\text{K}$ ), of the challenge molecule. The compounds represented on this graph are a variety of fluoro/hydrocarbons, and both polar and non-polar species are present. Because of such successful correlations, we have undertaken an analysis of the boiling points of a large range of organic compounds. In particular, we have attempted to analyze them in terms of dispersion, polarization and electrostatic interactions which could be simply related to the polarizability, dipole moment and size of the molecules.

Figure 1

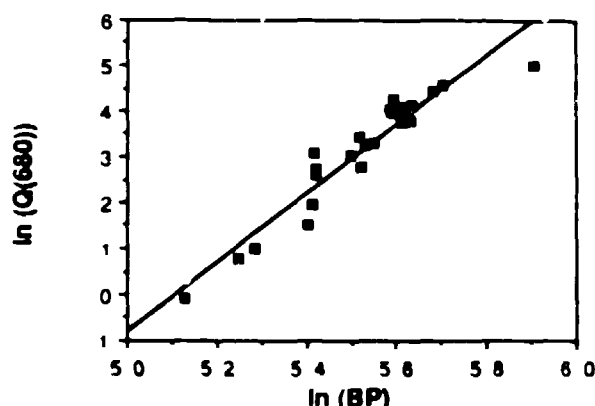
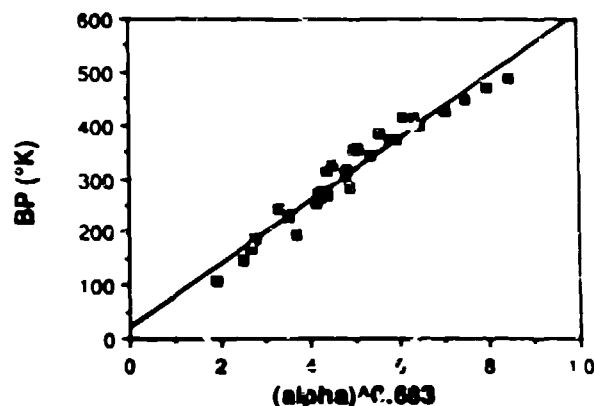


Figure 2



**Dispersion.** For strictly non-polar molecules, the only attractive interaction is that of dispersion. The standard formulation for the interaction between two atomic species, given by London, is shown in eq. 1.<sup>3</sup> Here,  $\alpha_a$  and  $\alpha_b$  are the polarizabilities of atoms a and b,  $r_{ab}$  is the

$$(1) \quad E_d = \frac{3}{4} \frac{\alpha_a \alpha_b}{r_{ab}^6} \frac{IP_a IP_b}{IP_a + IP_b}$$

distance between the centers of the atoms, and  $IP_a$  and  $IP_b$  are the ionization potentials of a and b. To extend this molecular systems, a simple approach would be to replace the atomic quantities with molecular quantities. That is, in place of  $\alpha_a$  would be  $\alpha_A$ , the polarizability of molecule A. A more sophisticated approach is to do a summation over the pairwise interactions between all atoms in molecule A with those in molecule B. This requires the definition of atomic polarizabilities within each molecule, though the IP's are taken as the molecular IP's.

We have attempted to use this equation directly with the molecular polarizability and diameter. The molecular polarizabilities and ionization potentials are given in standard sources.<sup>4</sup> The distance between molecular centers was taken as the average diameter of the molecule, which was determined from the molecular volumes. This was either calculated from the density of the liquid,<sup>4</sup> or from the "van der Waals" volumes of the constituent functional groups given by Bondi.<sup>5</sup> This simple analysis was found to work quite well for the mono- and diatomic gases, and even for  $\text{CH}_4$  and  $\text{CF}_4$ . However, larger molecules like  $\text{CMe}_4$  deviate substantially from this correlation.

The failure of  $\text{CMe}_4$  and other large molecules to fit this simple correlation illustrates the need to consider the dispersion interaction as a sum of pairwise atomic terms rather than on simply a molecular basis. In particular, we found that the boiling point of  $\text{CMe}_4$  is much higher than the simple molecular correlation predicts which indicates that the dispersion interaction must be much greater than predicted. When eq. 1 is recast as a summation over atomic terms, the origin for this is readily apparent. Because of the  $1/r^6$  weighting, the atoms at the surfaces of the molecules, where contact occurs, are responsible for the major part of the interaction. Further, since the distances between these surface atoms are much smaller than the center-to-center molecular distance, the dispersion interaction is calculated to be much larger

by this approach.

However, this rigorous approach of evaluating the dispersion interaction is somewhat tedious to effectively employ in this situation of boiling points correlations because a large number of different intermolecular orientations should really be examined to arrive at some sort of average interaction energy. Consequently, we have also explored various empirical relationships for non-polar organic molecules (those with  $\mu \leq 0.5$  D). Amazingly, we found a very simple linear relationship between  $\ln(\text{BP})$  and  $\ln(\alpha)$  as shown in eq 2 which has a

$$(2) \quad \ln(\text{BP}) = 0.683 \ln(\alpha) + 4.153$$

correlation coefficient of  $r = 0.973$  and  $\sigma = 0.053$ . This relationship can be expressed alternately as shown in eq 3 and a plot of this is given in Figure 2. The 37 compounds

$$(3) \quad \text{BP} = 63.65 \alpha^{0.683}$$

included in this correlation are a rather diverse group: straight-chain alkanes from methane to dodecane as well several branched and cyclic alkanes; simple alkenes (up to  $\text{C}_7$ ); benzene, toluene and the xylenes; and several perfluoro-alkanes and alkenes. Considering the great structural diversity of these compounds, this high level of correlation based on a single molecular parameter is quite outstanding. What is even more amazing is that non-polar inorganic compounds ranging from He to  $\text{UF}_6$  also follow a similar relationship, though these were not included in the present correlation.

From eq. 1, we would expect that the molecular size and ionization potential should make some contribution to the boiling point. The absence of a contribution from the ionization potential is not surprising since it does not vary dramatically for organic compounds (10-12 eV).<sup>4</sup> The inclusion of the molecular diameter resulted in the relationship given in eq 4 with a

$$(4) \quad \ln(\text{BP}) = 0.960 \ln(\alpha) - 0.920 \ln(d) + 5.104$$

correlation coefficient of  $r = 0.982$  and  $\sigma = 0.044$ . This represents only a slight improvement in the quality of the fit despite the appearance of a substantial contribution from the  $\ln(d)$  term. This can only occur if  $\ln(\alpha)$  and  $\ln(d)$  are highly correlated, which they are. The relationship between is shown given in eq. 5 ( $r = 0.921$ ,  $\sigma = 0.17$ ) based on the data for 126 organic

$$(5) \quad \ln(\alpha) = 3.519 \ln(d) - 3.693$$

compounds (both polar and non-polar).

Equation 5 leads to several interesting observations. The first is that the molecular polarizability increases only slightly faster than the molecular volume (which goes as  $d^3$ ). This means that the polarizability of these compounds per unit volume is close to constant. This is manifested by the fact that the refractive indices (which are a measure of the polarizability per volume) of these compounds do not vary substantially. Since the charcoal surface will be predominantly organic in nature, this suggests that we probably do not need a high level of sophistication to accurately characterize dispersion interactions with it. The second interesting point is that eqs 5 and 2 can be combined to give the relationship  $\text{BP} = A \alpha^2/d^{4.6}$  which is not far removed from the simple relationship expected from eq 1 of  $\text{BP} = A \alpha^2/d^6$  (where  $A$  is a proportionality constant). The reduction in the exponent of  $d$  probably has to do with the fact that only the atoms on the surface of the molecule are predominantly involved in the dispersion interaction. This point will probably be made clear by more sophisticated analyses.

These correlations with the boiling point imply that the energy of the dispersion interaction can be simply related to the polarizability of the molecule. Therefore, simple methods of calculating molecular polarizability become rather important. It has long been known that the molar refractivity of a compound (which is usually determined from the refractive index of the

liquid) can be readily approximated as a sum of atomic refractivities where an atom's refractivity will be somewhat dependent upon its bonding environment.<sup>6</sup> It directly follows from this that the spherically averaged molecular polarizability should be expressible as a sum of atomic polarizabilities. (These atomic polarizabilities would be required to evaluate the dispersion interaction by a sum of pairwise atomic terms.) We have analyzed the reported polarizabilities of 150 organic compounds by such a scheme to determine the atomic polarizability contributions given in Table 1. The correlation between calculated and observed polarizabilities is shown in Figure 3 and is quite good ( $r^2 = 0.966$ ,  $\sigma = 0.60$ ). We refer to the values given in the table as atomic polarizability contributions rather than directly as atomic polarizabilities because there are high correlations within these values (particularly between the values for H and C). This does not effect the ability to calculate the molecular polarizability, however. More sophisticated analyses are required to refine these as true "atomic" polarizabilities. We note in particular that the interactions between the induced dipoles on the various atoms of the molecule need to be included as detailed by Applequist, et al.<sup>7</sup>

TABLE 1

Polarizability Contributions ( $\text{\AA}^3$ ) of Various Functional Groups.

H-(C)	0.224	C(sp <sup>3</sup> )	1.432	C=O	2.108	O(sp <sup>3</sup> )	0.803
H-(N)	0.494	C(sp <sup>2</sup> )	1.756	C≡N	3.150	N(sp <sup>3</sup> )	1.429
H-(O)	0.201	C(sp)	1.584	NO <sub>2</sub>	3.643	N(ar)	0.897
F	0.498	C(ar)	1.539	ONC	3.014		

Figure 3

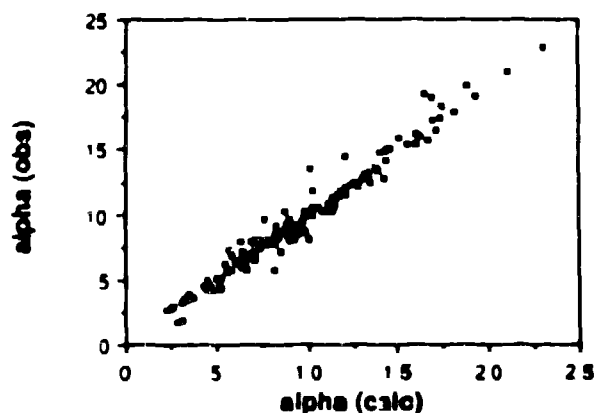
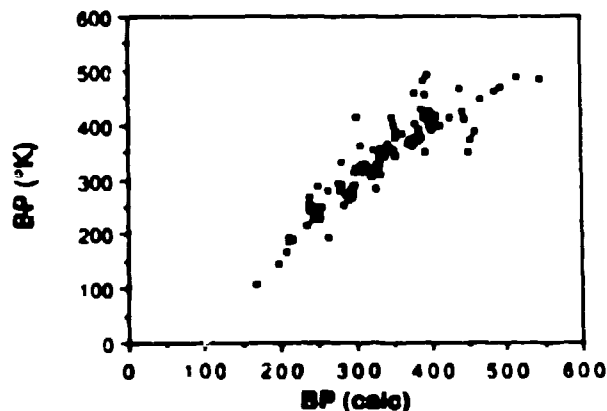


Figure 4



**Polarization.** The boiling points of polar molecules are all higher than they are predicted to be based solely on dispersion interactions, some by as much as 300°K. This clearly indicates that the polarization and electrostatic forces play an important role in the intermolecular interaction. To further delineate these effects, we approximate these molecules as consisting of point dipoles centered inside of polarizable spheres. The polarization and electrostatic energies of interaction between two molecules can be expressed as shown in eqs 6 and 7, respectively.

$$(6) \quad E_{\text{pol}} = -K \alpha \mu^2 / d^6$$

$$(7) \quad E_{\text{es}} = -L \mu^2 / d^3$$

Here,  $\alpha$  is the molecular polarizability,  $d$  is the average molecular diameter and distance between molecular centers, and  $\mu$  is the dipole moment of the molecule.  $K$  and  $L$  are geometric factors which depend upon the relative orientation of the dipole moments. Their values are on the order of unity.

Since we have shown above that  $\alpha \propto k d^3$ , we will be unable to distinguish between the separate effects of  $E_{pol}$  and  $E_{es}$  because the two values are very highly correlated. Therefore in correlations with boiling point we will use only one of these terms. We have selected to use  $E_{pol}$  because this term is always present whereas the effect of  $E_{es}$  could be minimized by rapid rotations of the molecules and by interference effects from several neighbors. Combining this with the term  $\alpha^{0.683}$ , which was determined above as a model for the dispersion forces, we arrive at the relationship shown in eq 8 and illustrated in Figure 4. This is based on data for

$$(8) \quad BP = 53.67 \alpha^{0.682} + 16070 \alpha \mu^2 \cdot d^6 + 63.05$$

104 organic compounds, and the overall fit is reasonably good ( $r = 0.913$ ,  $\sigma = 32.6^\circ K$ ).

The compounds used in this correlation, although ranging from non-polar to very polar ( $\mu = 4D$ ), did not include classes of compounds that strongly hydrogen-bond: alcohols, carboxylic acids and amides. These compounds were all found to have significantly higher boiling points than this model predicts. Our explanation of this is that the hydrogen bonding interaction is not adequately represented by a dipole in a sphere model, although we show in the next section that this interaction is essentially electrostatic in nature. Overall, we find that the boiling point of a molecule can be reasonably well predicted from its polarizability, size and dipole moment.

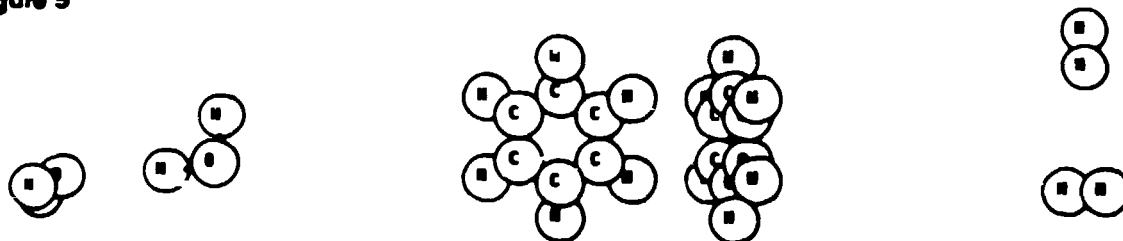
**Electrostatic Interactions.** For a more exact description of the electrostatic interactions, we use the technique of atom centered multipole expansions (ACME's).<sup>8</sup> First, the electron density distribution of a molecule is calculated using *ab initio* methods (Gaussian 82), typically at the 3-21G or 6-31G level. This distribution is then described in terms of an expansion of multipole moments centered on each atom of the molecule. Summation through the octapole moments provides an accurate portrayal of this charge distribution at distances beyond the typical van der Waals radii of the component atoms. Contained within this description is the basic charge distribution of the molecule (including the dipole, quadrupole, etc. moments), the location of  $\pi$ -bond and lone pairs of electrons, and the location of positively charged sites that may interact with these. This non-homogeneity of the electron density distribution then gives rise to electrostatic interactions between two molecules.

The power and utility of such a detailed description of the electron distribution are illustrated with three examples of the structures of the dimers of water, benzene and hydrogen. The three structures shown in Figure 5 are the minimum energy conformers determined solely from a consideration of electrostatic interactions, where the atoms are represented by "firm" spheres with the appropriate van der Waals radii.<sup>5</sup> (A steep exponential repulsive potential is used in place of a true hard sphere so as to allow the optimization routines to run smoothly.) The structure of the water dimer can be basically described as a hydrogen bond between the proton of one water and an oxygen  $sp^3$  lone pair. This calculated geometry is in very good agreement with the observed structure of the water dimer in the gas phase.<sup>9</sup> Further, the energy of interaction (6.9 kcal/mol) is in very good agreement with both the experimental heat of association (4.6-6.9 kcal/mol) as well as the value calculated from very high level *ab initio* treatments of the water dimer (4.5-5.4 kcal/mol).<sup>9</sup> This agreement results because the dispersion, polarization and exchange interactions tend to cancel each other out. This illustrates that the hydrogen bond is essentially electrostatic in nature and that it can be treated accurately with this technique.

The dimers of benzene and hydrogen illustrate that electrostatic interactions make important contributions in determining the geometries of systems that would typically be described as non-polar. (Electrostatic interactions must be present in any system consisting of non monoatomic molecules.) In benzene (as in other hydrocarbons), the hydrogen atoms carry a small net positive charge (+0.05) and the carbon atoms exhibit a small negative charge (-0.05). The T-shape of the benzene dimer results from the association of the positively charged hydrogens of one benzene with the negative  $\pi$ -system of the other while maximizing the distance between the two  $\pi$ -systems. This geometry is observed experimentally for the gas phase dimer and is particularly interesting because the consideration of only dispersion

interactions would lead to the prediction of a sandwich type structure.<sup>10</sup> The energy of interaction calculated here (0.84 kcal/mol) is again similar to the experimental and other calculated values. In hydrogen, there is a concentration of the electron density between the two nuclei leaving the ends of the molecules with a positive charge. The T-shape of the dimer then results from the positive end of one molecule approaching the negative center of another. The energy of interaction is not very great (0.05 kcal/mol), but this type of interaction is observed for the solid state structures of several diatomic species.

Figure 5



This use of ACME's to accurately represent electrostatic interactions is relatively inexpensive computationally. Although it may require an hour of Cray computation time to generate the ACME's of a molecule the size of benzene, including the SCF calculations, the optimization of the electrostatic interaction between two systems that contain on the order of one hundred atoms can be accomplished in several seconds. Further, the ACME's can be transferred on an atom by atom basis so that models for macromolecules or surfaces can be constructed from the ACME's of appropriate smaller molecules.

We are currently pursuing this route to develop a structured model of the charcoal surface. As a first order model, we are simply using a graphitic plane. The ACME's for the carbon atoms are taken to be similar to those of the central carbons of the polyacenes naphthalene and pyrene. The charges and dipole moments of the carbons in the polyacenes are small, non-zero quantities because of the presence of the hydrogen atoms. These quantities are set equal to zero for the carbons in the graphitic plane on the basis of symmetry. (There could be some net surface charge and dipole moment normal to the surface, but we have not attempted to include this.) The carbons do have appreciable quadrupole moments because the formation of  $\sigma$  and  $\pi$  bonds tends to pull the electron density away from the nuclear center. Overall, this basic surface will interact only weakly in an electrostatic sense. As a primitive model for the presence of heteroatoms, we set the charge of one of the carbons in the plane at  $\pm 0.25$ . This is on the order of the charge separation that is developed in polar functionalities such as ketones or nitriles.

The electrostatic energies of interaction of several molecules were calculated with this model and the results are summarized in Table 2. The results in column I are the results for the interaction with an electrically neutral carbon plane. The energies are non-zero because that carbon atoms do have a net quadrupole moment as mentioned above, but the net interactions are rather small. The results in column II are obtained when a  $+0.25$  charge is placed on one of the carbon atoms, and the results in column III are for a  $-0.25$  charge being placed on one of the carbon atoms. The interaction energies with the polar molecules  $C_2HF_3$  and  $H_2O$  are rather substantial (2-4 kcal/mol) as would be expected. What is more interesting is that the interaction energies with the "non-polar"  $C_2H_4$  and  $C_2F_4$  are also appreciable (0.5-1.7 kcal/mol). The interaction with  $H_2$  is quite small (0.2 kcal/mol), but this is much greater than if no charges are present.

We emphasize that these results only include pure electrostatic interactions. To include first order polarization effects, we take the polarizability of the carbons in the plane to be that of an  $sp^2$  carbon as given in Table 1. Both the energy required to polarize the carbon plane because of the presence of the electrostatic field of the adsorbate molecule, and the energy of interaction between this induced polarization field of the plane and the electrostatic field of the adsorbate molecule are included. However, the polarization of the adsorbate by either the

induced field of the surface or by charges embedded in the surface was not included. The energies of interaction with this polarizable and electrically neutral carbon plane are given in column IV, and these values should be compared with the results for the non-polarizable, neutral plane in column I. Again, substantial energies are found to result for the polar molecules with smaller, but non-zero, values resulting for the "non-polar" species.

TABLE 2

Calculated Interaction Energies (in kcal/mol) of Various Molecules with a Carbon Surface

Sorbate	I	II	III	IV
H <sub>2</sub>	-0.01	-0.14	-0.20	-0.01
C <sub>2</sub> H <sub>4</sub>	-0.13	-1.24	-0.45	-0.23
C <sub>2</sub> F <sub>4</sub>	-0.08	-0.56	-1.70	-0.44
C <sub>2</sub> HF <sub>3</sub>	0.38	-1.60	-2.22	-1.78
H <sub>2</sub> O	-0.87	-3.96	-3.78	-6.65

## CONCLUSIONS

We have demonstrated the separate roles of dispersion and of polarization/electrostatic interactions in determining the boiling points of a wide variety of organic compounds. By inference, this also demonstrates their importance in sorption behavior. The presence of charged impurities in a surface was shown to greatly enhance the binding of polar molecules to it, and to somewhat enhance the binding of non-polar species as well. Even in the absence of charge centers, the polarizability of the surface will enhance the binding of polar molecules.

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